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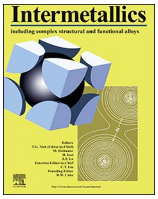

First-principles study of the structure, electronic, magnetic and elastic properties of half-Heusler compounds LiXGe (X = Ca, Sr and Ba)

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ABSTRACT

We first investigate the structural, electronic and magnetic properties of half-Heusler compounds LiXGe (X = Ca, Sr and Ba), by using the first-principles calculations within full-potential local-orbital minimum-basis method. The calculations show that all compounds are half-metallic ferromagnets with the same magnetic moment of 1.00 μ_B per formula unit and all compounds follow the Slater-Pauling rule: $M_{tot} = (8 - Z_{tot})\mu_B$. In the aspects of phonon dispersion, cohesive energy and formation energy, we found all the compounds are found to be stable. Our calculations also show that the half-metallicities can be preserved with lattice constants from −3.6% to 21.4%, −3.8% to 16.1% and −1.2% to 14.7% for LiCaGe, LiSrGe and LiBaGe. At the end the elastic properties for the all three compounds are also reported.

1. Introduction

Half-metallic ferromagnets (HMFs) are promising to next-generation spintronic devices due to their unique property: they have only one spin channel for conduction. It means that the spin-polarized band structure exhibits metallic behavior for one spin channel, while insulative or semiconductive behavior for the other spin channel [1]. Due to that special property, the density of states at the Fermi level have, theoretically, 100% spin polarization.

The first half-metallic material was the half-Heusler alloy NiMnSb which was introduced by de Groot [1]. HMFs have been widely found in rocksalft structure Src and Bac [2], zinc-blende CrAs [3]and CaC [4], double-perovskite compounds Mn2FeReO6 [5], Heusler alloys Zr2RhZ (Z = Al, Ga, In) [6] and half-Heusler. Among them, half-Heusler alloys are widely studied [7–10]. Half-Heusler alloys are known to combine with a wide variety of different elements. They get more and more attention of researchers due to different combinations of half-Heusler alloys, resulting a great variety of physical properties, such as the electrical special transport properties of TiCoSb [11] and the magnetic properties of the half-metallic ferromagnet NiMnSb [12]. Moreover, experiments indicated that the alloys with compositions in the vicinity of the ideal equiatomic composition can be prepared. So, searching for half-Heusler compounds with half-metallic is necessary and meaningful. It is of importance for theoretical computations to give reliable and useful information to synthesization in experiments where few half-metallic half-Heusler compounds have been synthesized now. In order to provide more guidances for HMFs applications, it is necessary to study their elastic properties, chemical stability and half-metallic stability.

The half-Heusler compounds RbSrX (C, Si and Ge) has been investigated [13]. And all the compounds RbSrX (C, Si and Ge) had been proved to be half metal. In this paper half-Heusler alloys LiXGe (X = Ca, Sr and Ba) have crystallized in the $C1_b$ structure, which consists of three interpenetrating face-centered cubic sublattices occupied by the three atoms Li, X (X = Ca Sr and Ba) and Ge. We theoretically explore the stability, elastic properties, electronic structure, magnetic properties and pressure dependency of LiXGe (X = Ca, Sr and Ba) with the half-Heusler structure.

The organization of this paper is as follow. In Section 2, we briefly describe our method of calculation. In Section 3, the crystal structure, phonon dispersion, electronic structure, magnetism, chemical stability, half-metallic stability and elastic properties of all alloys are discussed by the results we calculated. Section 4 summarizes the paper.

2. Method of calculations

In this paper, all the compands has been calculated by using the scalar relativistic version of the full-potential local-orbital (FPLO)

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minimum-basis band-structure method [14,15]. For the present calculations, the site-centered potentials and densities were expanded in spherical harmonic contributions up to $l_{\max} = 12$. The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) is used to discribe the exchange-correlation (XC) potential [16]. For the irreducible brillouin zone, the $20 \times 20 \times 20$ k meshes in the Brillouin zone have been used for all the calculations. The convergence criteria of self-consistent iterations is set to 10^{-6} to the density and 10^{-8} Hartree to the total energy per formula unit. And we also calculated the phonon dispersion by using the Cambridge sequential total energy package (CASTEP) code [17,18].

3. Results and discussions

3.1. Crystal structure and phonon dispersion

The half-Heusler compounds (general formula: XYZ) crystallize in a non-centrosymmetric cubic structure (space group No. 216, $F\overline{4}3m$, $C1_b$) which is a ternary ordered variant of the CaF_2 structure and can be derived from the tetrahedral ZnS-type structure by filling the octahedral lattice sites. This structure consists of three interpenetrating fcc sublattices, each of which is occupied by the X, Y and Z atoms [19].

As we know, half-Heusler structure has three inequivalent atomic arrangements (Table 1). Before we calculating, the inequivalent atomic arrangement must be determined. The spin-polarization (FM phase) and non-spin-polarization (NM phase) total energies are calculated for all compounds in Type 1, Type 2 and Type 3 structures whitch can be seen at (Table 2). By observing the value of the energy which can clearly be seen in Fig. 1, it is found that the lowest energy corresponds to the spin-polarization (FM phase) in Type 1 for the three compounds. In the other word the spin-polarization (FM phase) in Type 1 structure is the most stable one for the all compounds LiXGe (X = Ca, Sr and Ba). And the lattice constants of equilibrium we obtain are 6.860, 7.178 and 7.490 Å for LiCaGe, LiSrGe and LiBaGe, respectively.

Phonons play a major role in many of the physical properties of solids, such as the electrical conductivities, materials thermal, superconducting temperature, Debye temperature and structural stability. In this paper, We discuss structural stability through phonon dispersion. The vibration frequency is a function of the wave vector k, which can be written with the dispersion relation [20]:

$$\omega(k) = \sum_j \omega_j(k) \tag{1}$$

Due to the translational symmetry:

$$\omega_j(k) = \omega_j(k + G) \tag{2}$$

we could only calculate the phonon frequencies in the first Brillouin zone (BZ). The primitive cell of LiXGe (X = Ca, Sr and Ba) has three atoms, suggesting that the spectrum should have 9 lines. And all the lines have been shown in Fig. 2. Moreover, their calculated phonon dispersion curves do not contain soft modes at any high-symmetry direction, which indicates the stabilities of the LiXGe (X = Ca, Sr and Ba) [17].

3.2. Electronic structure and magnetic properties

In this subsection the electronic structure and magnetic properties are discussed, which are very importance to the alloys and are the core of my present work. The properties are calculated, based on the ferromagnetic equilibrium lattice structure. The calculated total spin magnetic moment, band gap and spin-flip gap are tabulated in Table 3.

Table 1
Inequivalent site occupancies within the $C1_b$-type structure for LiXGe (X = Ca, Sr and Ba).

	4a (X)	4b (Y)	4c (Z)
Type 1	(1/4,1/4,1/4)	(3/4,3/4,3/4)	(0,0,0)
Type 2	(0,0,0)	(3/4,3/4,3/4)	(1/4,1/4,1/4)
Type 3	(1/2,1/2,1/2)	(3/4,3/4,3/4)	(0,0,0)

Table 2
Calculated the total energies (Hartree) of nonmagnetic (NM) and ferromagnetic phase (FM) of LiXGe (X = Ca, Sr and Ba) on the three types.

	LiCaGe	LiSrGe	LiBaGe
Type1-FM(Hartree)	−2787.0446	−5286.49776	−10246.0309
Type1-NM(Hartree)	−2787.0433	−5286.49430	−10246.0305
Type2-FM(Hartree)	−2787.0419	−5286.49470	−10246.0276
Type2-NM(Hartree)	−2787.0419	−5286.49470	−10246.0276
Type3-FM(Hartree)	−2787.0033	−5286.45233	−10245.9862
Type3-NM(Hartree)	−2787.0033	−5286.45035	−10245.9862

In Figs. 3–5, we display the band structures of LiXGe (X = Ca, Sr and Ba) alloys. It can be seen the majority-spin (spin-up) states show semiconductive character while the minority-spin (spin-down) ones show metallic nature. The band gap is formed by the valence band maximum (VBM) and the conduction band minimum (CBM). The spin-flip gap is defined as the required energy by which electrons of VBM are reversed. In Table 3, we offer the band gap and spin-flip gap. All the three compounds have a large band gap. Meanwhile, LiSrGe also has a large half-metallic (spin-flip) gap which larger half-metallic gaps mean higher Curie temperatures [21].

To further explain the electronic band structure, we have also calculated the total density of states (DOS) and partial DOS for LiXGe (X = Ca, Sr and Ba), displayed in Figs. 6–8, respectively. In Fig. 5, we can see that for LiCaGe near the Fermi level the total DOS are mainly contributed by the 4p states of Ge, 2p states of Li and 3d states of Ca. And the most contribution is the 4p states of Ge. For LiSrGe as can be seen from Fig. 6, around the Fermi level, the total DOS are mainly contributed by the 4p states of Ge, 2p states of Li and 4d states of Sr. And the most contribution is the 4p states of Ge. We can also see that there are hybridizations between Li-2p state and Sr-4d state around the Fermi level. Fig. 8 shows the calculated results of total DOS and partial DOS of LiBaGe. Fig. 8 shows the total DOS of LiBaGe are mainly contributed by the 4p states of Ge, the 2p states of Li and the 4d states of Ba near the Fermi level, of which the most contribution is the 4p states of Ge.

In Table 3, we found that the total spin magnetic moments are 1 μ_B for all alloys, which is one of unique properties of half-metallic systems. The cause of 1 μ_B is due to the four majority-spin and three minority-spin in occupied states around the Fermi level. And the total spin magnetic moments follow the Slater-Pauling rule:

$$M_{tot} = (8 - Z_{tot})\mu_B, \tag{3}$$

where M_{tot} is the total spin magnetic moment, and Z_{tot} is the total number of valence electrons. The total number of valence electrons for LiXGe (X = Ca, Sr and Ba) is 7.

In this subsection, we investigate the electronic structure and magnetic properties for LiXGe (X = Ca, Sr and Ba) and all results are in Table 3. We find that all of the compounds have a half-metallic nature.

3.3. Chemical stability and half-metallic stability

Firstly, in this section, we investigate the formation energy and cohesive energy of the three compounds to see their stability in existence and chemical synthesis for applications. The formation energy is defined by the following equation [22]:

$$\Delta H_{LiXGe} = E^{LiXGe} - E_{bulk}^{Li} - E_{bulk}^{X} - E_{bulk}^{Ge}, \tag{4}$$

where E^{LiXGe} are the total energies of the LiXGe (X = Ca, Sr and Ba) alloys, E_{bulk}^{Li}, E_{bulk}^{X} (X = Ca, Sr and Ba) and E_{bulk}^{Ge} are the chemical potential of the bulk of the element. In general, a negative value of